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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the two-layer structure particle state constituent which can be conveniently used as positive active material in a rechargeable lithium-ion battery, and the rechargeable lithium-ion battery which uses it.

[0002]

[Description of the Prior Art]Lithium nickel complex oxide is one of the materials which attract attention as high power and a high energy density battery in recent years as positive active material in the rechargeable lithium-ion battery currently used for a notebook sized personal computer, PHS, a cellular phone, etc., for example. this lithium nickel complex oxide -- "composition of the spherical  $\text{LiCoO}_2$  pulverized coal by an ultrasonic atomization thermal decomposition method, and application to the active material for lithium secondary batteries" (Takashi Hagiwara.) Yoshihiko Saito, the Yanagawa \*\*\*\*, Nobuo Ogata, Kokichi Yoshida, Masayuki Takashima, Susumu Yonezawa, Yasuharu Mizuno, Norifumi Nagata, Kenji Ogawa, journal OBU the ceramic society OBU Japan (Journal of the Ceramic Society of Japan), It is  $\text{LiMO}_2$  (M among a formula) as indicated to the 101st volume and the 1159-1163rd page (1993). they are Cr, Mn, nickel, Fe, Co, or V. a group expressed -- it is one of the compounds, and like  $\text{LiCoO}_2$ , since charge and discharge voltage is high especially, it is dramatically useful as positive active material.

[0003]In order to face as positive active material of a rechargeable lithium-ion battery using such lithium nickel complex oxide and to improve the performance, that to which the presentation of lithium nickel complex oxide was changed, and the thing which has improved the physical property of lithium nickel complex oxide are proposed.

[0004]As that to which the presentation of lithium nickel complex oxide was changed, it is

$\text{Li}_x\text{MO}_2$  (M shows a transition metal.) to JP,4-328278,A. It is expressed with  $0.05 \leq x < 1.10$ , and that whose  $\text{LiCO}_3$  content is 0.5 to 15 % of the weight is indicated.

[0005]To JP,6-150929,A,  $\text{LiNiO}_2$  containing at least one sort in Na and K is indicated. To JP,62-256371,A, JP,5-36411,A, and JP,7-307150,A,  $\text{LiNiO}_2$  containing elements, such as Co, V, Cr, Fe, P, B, Si, Mo, and W, is indicated. As what has improved the physical property of lithium nickel complex oxide, the  $\text{LiNiO}_2$  particles which a primary particle turns into from the set particles more than secondary [ of 1 micrometer or less ] are indicated by JP,7-10590,A. When this  $\text{LiNiO}_2$  particle is used for the positive active material of a rechargeable lithium-ion battery, it excels in reproducibility and it is indicated that the amount of high charges and discharges can be obtained.

[0006]However, even if it is the cell manufactured using the lithium nickel complex oxide improved by doing in this way, When it is neglected in the car which has stopped the cellular phone which carries the above-mentioned cell in the daytime [ of midsummer ], for example when this is neglected to a hot environmental atmosphere for a long time, the lithium nickel complex oxide and nonaqueous electrolyte of positive active material react, Some nonaqueous electrolyte decomposes and gasifies, battery container internal pressure rises, a cell explodes, and a cell wearing equipment breakdown etc. cause a fire, and there is danger of soiling environment.

[0007]Then, in order to solve such a problem, to JP,8-138670,A. The nonaqueous solvent secondary battery using what used the surface layer of lithium-nickel-complex-oxide ( $\text{LiNiO}_2$ ) powder as the layer with high concentration of a transition element of a different kind like cobalt as positive active material of a rechargeable battery is proposed. However, the concentration of the different species element which exists in the surface layer of a powder particle, for example, cobalt, is low like the lithium-nickel-complex-oxide powder shown in the example of the above-mentioned gazette, the atomic ratio to nickel of a different species element is 0.2 or less, and solution of the problem mentioned above is not yet enough.

[0008]

[Problem(s) to be Solved by the Invention]This invention was made in order to solve a problem in conventional lithium nickel complex oxide which was mentioned above, and it is \*\*\*\*. If the rechargeable lithium-ion battery which is a particle state constituent which has the two-layer structure which consists of a lithium multiple oxide with which the metal kind which constitutes the purpose is mutually different, and uses this as positive active material is constituted, This cell is providing the lithium compound-oxide-particles-like constituent which can suppress disassembly of nonaqueous electrolyte to the minimum, and the rechargeable lithium-ion battery which uses this, also when it holds to an elevated temperature.

[0009]When the rechargeable lithium-ion battery which uses lithium-nickel-complex-oxide particles as positive active material is held more at an elevated temperature in details, The decomposition reaction of nonaqueous electrolyte occurs by the interface of the particles of the active material, and nonaqueous electrolyte, cracked gas is emitted, the pressure in a battery container rises, and a possibility that a cell may explode arises. Then, what is necessary is for what is necessary to be just to make the interface of an active material particle and nonaqueous electrolyte as small as possible, and just to make specific surface area of an active material particle as small as possible, in order to control disassembly of this nonaqueous electrolyte. However, generally, when making small specific surface area of an active material particle, charge-and-discharge capacity falls, and the fault that the response of charge and discharge falls is also produced. Therefore, they were important requirements when using the active material particle which has the specific surface area from which the battery characteristic which the balance of these characteristics was able to take is obtained manufactured a rechargeable lithium-ion battery.

[0010]However, this invention persons find out the particle state constituent for active materials excellent in high temperature oxidation stability for rechargeable lithium-ion batteries regardless of the specific surface area of an active material particle, and result in this invention.

[0011]

[Means for Solving the Problem]A two-layer structure particle state constituent by this invention is provided with a central layer which consists of lithium nickel complex oxide, a lithium cobalt multiple oxide, or a becoming surface layer, and the cobalt/(nickel + cobalt) atomic ratio in 0.1-micrometer Fukashi are in the range of 0.2-1 from the surface.

[0012]Especially in this invention, a central layer is general formula (I).

$\text{Li}_p \text{nickel}_{1-x} \text{A}_x \text{O}_y$  (A among a formula) At least one sort of elements chosen from a group which consists of B, Mg, aluminum, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nb, Hf, Ta, and Pb are shown. p shows the number of the ranges of 0.90-1.10, x shows the number of the ranges of 0-0.25, and y shows the number of the ranges of 1.825-2.3. It consists of lithium nickel complex oxide expressed, and a surface layer is general formula (II).

$\text{Li}_q \text{Co}_{1-a} \text{Z}_a \text{O}_b$  (Z among a formula) At least one sort of elements chosen from a group which consists of B, Mg, aluminum, Si, Sc, Ti, V, Cr, Mn, Fe, nickel, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb are shown. q shows the number of the ranges of 0.90-1.10, a shows the number of the ranges of 0-0.25, and b shows the number of the ranges of 1.825-2.3. It is preferred to consist of lithium nickel complex oxide expressed.

[0013]A two-layer structure particle state constituent which was mentioned above is used for a

rechargeable lithium-ion battery by this invention as positive active material.

[0014]

[Embodiment of the Invention]The two-layer structure particle state constituent by this invention is explained in detail below. The particle state constituent by this invention is a particle state constituent which consists of two-layer [ of a central layer and a surface layer ], a central layer consists of lithium nickel complex oxide, and a surface layer consists of lithium cobalt multiple oxides. However, in the range which does not have influence harmful to a battery characteristic, the central layer and the surface layer may have other oxides and multiple oxides, respectively.

[0015]As long as the two-layer structure particle state constituent by this invention has two-layer structure, it may be what kind of shape, For example, the aggregate of the primary particle which consists of each multiple oxide may be sufficient as the above-mentioned central layers and surface layers, or these both besides what has the structure where the surface layer which consists of lithium cobalt multiple oxides covers the central layer which is a primary particle which consists of lithium nickel complex oxide. Although the substantially spherical thing of the shape is preferred, it may be a cube-like substantially and other shape may be sufficient as it, so that it may mention later.

[0016]Although they are not limited, when using as positive active material of a rechargeable lithium-ion battery, especially the shape and the size of the above-mentioned particle state constituent by this invention are 3-100 micrometers in mean particle diameter, and their substantially spherical thing is preferred. Thus, when a particle state constituent is substantially spherical, it excels in restoration nature, namely, since pack density can be enlarged, it is desirable. When the mean particle diameter is less than 3 micrometers, When it uses as positive active material of a rechargeable lithium-ion battery, and the electric capacity per unit capacity of a cell becomes low and another side and mean particle diameter exceed 100 micrometers since the filling factor is low, Since there is a possibility that the particle may penetrate the separator which consists of a porous film of polymers, such as polypropylene, for example, and may produce a short circuit between an anode and a negative electrode, it is not desirable. The range especially of the size of the particle state constituent by this invention is 3-50 micrometers, and the range of it is 5-30 micrometers most preferably.

[0017]However, the above-mentioned particle state constituent which has the shape except spherical may be used as positive active material for rechargeable lithium-ion batteries if needed. The central layer consists of lithium nickel complex oxide, and the particle state constituent by this invention is general formula (I) preferably.

$\text{Li}_p\text{nickel}_{1-x}\text{A}_x\text{O}_y$  (A among a formula) At least one sort of elements chosen from the group which consists of B, Mg, aluminum, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nb, Hf, Ta, and Pb are shown. p shows the number of the ranges of

0.90-1.10, x shows the number of the ranges of 0-0.25, and y shows the number of the ranges of 1.825-2.3. It consists of lithium nickel complex oxide expressed.

[0018]On the other hand, the surface layer consists of lithium cobalt multiple oxides, and the particle state constituent by this invention is general formula (II) preferably.

$\text{Li}_{1-q}\text{Co}_{1-a}\text{Z}_a\text{O}_b$  (Z among a formula) At least one sort of elements chosen from the group which consists of B, Mg, aluminum, Si, Sc, Ti, V, Cr, Mn, Fe, nickel, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Sn, Sb, La, Ce, Pr, Nd, Hf, Ta, and Pb are shown. q shows the number of the ranges of 0.90-1.10, a shows the number of the ranges of 0-0.25, and b shows the number of the ranges of 1.825-2.3. It consists of a lithium cobalt multiple oxide expressed.

[0019]In the above-mentioned general formula (I) and (II), the conservation characteristic of a cell can be further improved by using a particle state constituent which has x or a in the range of 0-0.25 as positive active material in a rechargeable lithium-ion battery. However, when x or a exceeds 0.25, since the charge-and-discharge capacity of a cell is reduced greatly, it is not desirable.

[0020]The two-layer structure particle state constituent by this invention consists of a surface layer which consists of a central layer which consists of lithium nickel complex oxide, and a lithium cobalt multiple oxide, as mentioned above, Although it tends to disassemble nonaqueous electrolyte into it at an elevated temperature although lithium nickel complex oxide has the high charge-and-discharge capacity of 190 or more mAh/g here, another side and a lithium cobalt multiple oxide have charge-and-discharge capacity lower than lithium nickel complex oxide and it is about 150 mAh/g, Even if held at an elevated temperature, it is hard to make nonaqueous electrolyte disassemble. In this way, the particle state constituent by this invention uses only the advantage which two lithium multiple oxides have, and it combines it so that a fault may be compensated.

[0021]Namely, when the above-mentioned two-layer structure particle state constituent by this invention is used as positive active material of a rechargeable lithium-ion battery, Only the lithium cobalt multiple oxide of a surface area layer contacts nonaqueous electrolyte, and this lithium cobalt multiple oxide, Since it is hard to disassemble nonaqueous electrolyte also when held at an elevated temperature as mentioned above, it contributes to the stability of a cell, and the above-mentioned two-layer structure particle state constituent has lithium nickel complex oxide with large charge-and-discharge capacity as a central layer further, therefore it has high charge-and-discharge capacity as a whole.

[0022]In this way, when using the two-layer structure particle state constituent by this invention as positive active material of a rechargeable lithium-ion battery, it excels in high temperature oxidation stability, and the rechargeable battery which has high charge-and-discharge capacity can be obtained.

[0023]In this invention, especially the quantitative ratio of a surface layer and a central layer

increases the ratio of a central layer, when it is not limited and thinks charge-and-discharge capacity as important, when thinking high temperature oxidation stability as important, it should just increase the ratio of a surface layer and arbitrary ratios can be used for it with the target battery characteristic. However, in the two-layer structure particle state constituent by this invention, The sum of the atomic number of the sum (Co+Z) of the atomic number of the cobalt atom of a surface layer, and Z atom, the nickel atom of a central layer, and A atom (nickel+A), Namely, a surface layer (the atomic ratio (nickel+A) of Co+Z)/central layer is in the range of  $5 / 100 - 50/100$ , and is usually in the range of  $10 / 100 - 30/100$  preferably.)

[0024]Although it is ideal in the two-layer structure particle state constituent by this invention to be thoroughly covered with the lithium cobalt multiple oxide as for the surface of particles, However, practically, when the cobalt/(nickel + cobalt) atomic ratio from a particle surface to a depth of 0.1 micrometer are in the range of 0.2-1, the stability of the cell made into the purpose can be obtained by using such a constituent as positive active material in a rechargeable lithium-ion battery. In particular, according to this invention, it is preferred that the cobalt/(nickel + cobalt) atomic ratio in 0.1-micrometer Fukushima are in the range of 0.3-1 from the above-mentioned particle surface, and it is still more preferred that it is in the range of 0.5-1.

[0025]In the two-layer structure particle state constituent by this invention, Although the ratio, i.e., Li/(nickel+A) atomic ratio, of the Li atom to the sum of Ni atoms and A atom is a stoichiometrical multiple oxide which is 1, i.e., the lithium nickel complex oxide expressed with said formula (I) is  $p = 1$ , usually, however, Li/(nickel+A) atomic ratio may be the nonstoichiometric multiple oxides which do not come out one. That is, p is the number of the ranges of 0.90-1.10.

[0026]In the two-layer structure particle state constituent according to this invention similarly, Although the ratio, i.e., Li/(Co+Z) atomic ratio, of the Li atom to the sum of Co atom and Z atom is a stoichiometrical multiple oxide which is 1, i.e., the lithium cobalt multiple oxide which is said formula (II) and is expressed is  $q = 1$ , usually, however, Li/(Co+Z) atomic ratio may be the nonstoichiometric multiple oxides which do not come out one. That is, q is the number of the ranges of 0.90-1.10.

[0027]The two-layer structure particle state constituent by this invention can be manufactured by the following methods, for example. According to such a manufacturing method, the two-layer structure particle state constituent by this invention which has the cobalt/(nickel + cobalt) atomic ratio in 0.1-micrometer Fukushima in the range of 0.2-1 can be obtained from the surface.

[0028](1) Prepare the particles which cover cobalt hydroxide on the surface of the particles of nickel hydroxide by adding to the slurry which distributed the powder of nickel hydroxide in water continuously, and making cobalt salt solution and caustic alkali solution react to it under existence of ammonium ion. The particle state constituent by this invention can be obtained by mixing and calcinating lithium hydroxide to this.

[0029](2) By the same method as the above, prepare the particles which cover cobalt hydroxide, oxidize this on the surface of the particles of nickel hydroxide, prepare hydrous oxidation nickel cobalt on it, and it ranks second to it, The particle state constituent by this invention can be obtained by performing lithium hydroxide and hydrothermal reaction for this in an aqueous dispersion medium and under high temperature high pressure.

[0030]A two-layer structure particle state constituent which was mentioned above is used for the rechargeable lithium-ion battery by this invention as positive active material.

[0031]An example of a rechargeable lithium-ion battery is shown in drawing 1. The anode 1 and the negative electrode 2 counter via the separator 3 impregnated with nonaqueous electrolyte, and are accommodated in the battery container 4, It is connected to the lead 6 for anodes via the positive pole collector 5, and the negative electrode 2 is connected to the lead 8 for negative electrodes via the negative pole collector 7, and the above-mentioned anode 1 is constituted so that the chemical energy produced inside the cell can be taken out from the above-mentioned leads 6 and 8 to the exterior as electrical machinery energy.

[0032]The particle state constituent by this invention blends and kneads a conducting agent, a binder, a bulking agent, etc. to this, uses them as a mixture, applies and sticks this to the positive pole collector which consists of stainless meshes by pressure, for example, carries out stoving under decompression, and let it be an anode. It is good also as an anode for disc-like etc. to carry out pressing of the above-mentioned mixture to shape suitably, and heat-treat it under a vacuum if needed.

[0033]It will not be limited especially if it is a electron conductive material which does not cause a chemical change in a rechargeable lithium-ion battery as the above-mentioned conducting agent, For example, natural graphite, an artificial graphite, carbon black, acetylene black, Ketchen black, carbon fiber, a metal powder, a metal fiber, a polyphenylene derivative, etc. can be mentioned. These may be used alone and may use two or more sorts together.

[0034]Although the loadings in particular of the above-mentioned conducting agent in the above-mentioned mixture are not limited, its 1 to 50 % of the weight is preferred, and 2 to 30% of the weight of its range is usually especially preferred. Especially, it is not limited by the binder, either but For example, starch, polyvinyl alcohol, Carboxymethyl cellulose, hydroxypropylcellulose, regenerated cellulose, Diacetyl cellulose, polyvinyl chloride, a polyvinyl pyrrolidone, tetrafluoroethylene, Polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene copolymer (EPDM), sulfonation EPDM, a styrene butadiene rubber, polybutadiene, fluorocarbon rubber, polyethylene oxide, etc. can be mentioned. These may be used alone and may use two or more sorts together. Although the loadings of the above-mentioned binder in a mixture are not limited in particular, either, it is 1 to 50% of the weight of a range, and is usually 2 to 30% of the weight of a range preferably.

[0035]a bulking agent is boiled and blended with positive active material if needed. If it is the

fibrous material which does not cause a chemical change in a rechargeable lithium-ion battery as a bulking agent, it is not limited in particular, for example, textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, etc. can be mentioned. Although the loadings of these bulking agents in a mixture are not limited in particular, either, 0 to 30% of the weight of the range is usually preferred.

[0036]In the rechargeable lithium-ion battery by this invention, as a negative electrode, if conventionally used for the rechargeable lithium-ion battery, it is not limited in particular, but the sheet like object and molded product which consist of lithium, a lithium alloy, stainless steel, nickel, copper, titanium, aluminum, baked carbon, etc. can be mentioned, for example.

[0037]It is usually formed on a charge collector at an anode and a negative electrode.

Especially as a charge collector, although not limited, stainless steel, its mesh, etc. are usually used.

[0038]As long as nonaqueous electrolyte is also known conventionally, any may be sufficient, but. For example, that in which dissociative lithium salt, such as lithium perchlorate, lithium, hexafluorophosphate, was dissolved can be mentioned into organic solvents, such as ether, such as carbonate, such as propylene carbonate, sulfolane, lactone, and 1,2-dimethoxyethane. Although the porous film etc. which consist of amount polymers of synthetic macromolecules, such as polypropylene, are used as a separator, for example, it is not limited to this.

[0039]

[Effect of the Invention]The two-layer structure particle state constituent by this invention is provided with the surface layer which consists of a central layer which consists of lithium nickel complex oxide, and a lithium cobalt multiple oxide, and. The cobalt/(nickel + cobalt) atomic ratio in 0.1-micrometer Fukashi are in the range of 0.2-1 from a particle surface, and such a two-layer structure particle state constituent is used for the rechargeable lithium-ion battery by this invention as positive active material.

[0040]Therefore, according to the rechargeable lithium-ion battery by this invention, nonaqueous electrolyte, Also when held at an elevated temperature, contact only the lithium cobalt multiple oxide of the surface layer which is hard to decompose for nonaqueous electrolyte, and another side and the above-mentioned particle state constituent, Having lithium nickel complex oxide with large charge-and-discharge capacity as a central layer, the above-mentioned particle state constituent has high charge-and-discharge capacity as a whole here. In this way, the rechargeable lithium-ion battery by this invention is excellent in high temperature oxidation stability, and it has high charge-and-discharge capacity.

[0041]The rechargeable lithium-ion battery by this invention, for example A notebook sized personal computer, It can use conveniently for medical equipment, such as electronic equipment, such as a cellular phone, a cordless phone cordless handset, a video movie, a



liquid crystal television, an electric shaver, a portable radio, a headphone stereo cassette tape recorder, a backup power supply, and a memory card, a pacemaker, and hearing aid, etc.  
[0042]

[Example] Although an example is given to below and this invention is explained to it, this invention is not limited at all by these examples. In the following examples, the amount of surface-layer elements / amount mole ratio of central layer elements by it are summarized in Table 1 and 2, and is indicated to be a charge (mol) of the transition element in each raw material used in order to prepare a central layer and a surface layer.

[0043] Under ammonium ion existence, in example 1 nickel-nitrate solution, sodium hydroxide solution was added continuously, it neutralized in it, and the aggregated particle powder in which primary particles gathered and which consists of spherical nickel hydroxide substantially was obtained. The specific surface area of this powder was  $148\text{m}^2/\text{g}$ . The scanning electron microscope photograph of this powder is shown in drawing 2.

[0044] This spherical nickel hydroxide 18.54g was distributed in the water 0.1L in the glass beaker of 1.0L capacity, and the slurry was obtained. Stirring, after adding cobalt nitrate solution (1.2mol/L) 17.0mL to this slurry under ammonium ion existence and sealing a beaker, nitrogen gas was comparatively boiled for 0.5L, it introduced into the slurry, and the nitrogen purge was performed. Sodium hydroxide solution (0.11mol/L) was added at a rate for 1.0mL/with the metering pump 30 minutes afterward for 8 hours. Thus, the obtained precipitation was filtered and rinsed, day desiccation was carried out at an electric drying in a plane and  $60^\circ\text{C}$ , and about 20 g of powder was obtained.

[0045] When this powder was analyzed by X-ray diffraction, as shown in drawing 3, only the peak of nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) was checked. The scanning electron microscope photograph of this powder is substantially consisted of spherical particles, as shown in drawing 4.

[0046] As shown in drawing 5, when line analysis of the particle section was conducted in EPMA (electron beam probe microanalyzer), it was checked that nickel is unevenly distributed in the particle central part, and cobalt is unevenly distributed in the particle layer part, respectively.

[0047] From the above analysis result, it was checked that the above-mentioned powder consists of nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) of crystallinity [central part], and that they are spherical particles substantially consist of cobalt hydroxide ( $\text{Co}(\text{OH})_2$ ) with an amorphous layer part.